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INTERVALENCE ELECTRON TRANSFER IN BICOBALTOCENE
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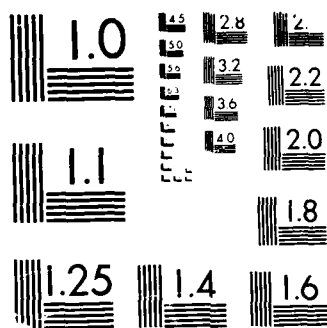
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Comparison with Biferrocenes

by

G. E. McManis, R. M. Nielson, and M. J. Weaver

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Intervalence Electron Transfer in Bicobaltocene Cations:

Comparison with Biferrocenes

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Abstract

The near-infrared absorption parameters for bicobaltocene monocation, $(\text{Cp}_2\text{Co})_2^+$, evaluated in several solvents, are compared with corresponding data for biferrocene cation, $(\text{Cp}_2\text{Fe})_2^+$, in order to ascertain the consequence of metal substitution upon the degree of redox-site electronic coupling. From the markedly (ca. 5 fold) larger intervalence band intensities, narrower bandwidths, and milder solvent dependence of the band energy observed for the former system, the degree of Co(III)-Co(II) electronic coupling is deduced to be substantially greater than for Fe(III)-Fe(II). A similar conclusion is reached from a comparison of near-infrared spectra for bis(fulvalene)-dicobalt and -diiron monocations. These differences are also reflected in more negative comproportionation free energies for the cobalt mixed-valence analogs, as derived from electrochemical data. These findings are consistent with orbital symmetry considerations, since electron transfer for the Co(III)-Co(II) system is expected to involve a ligand-centered $4e_{1g}$ orbital, as compared with strongly metal-localized $4e_2$ or $8a_{1g}$ orbitals that are apparently utilized in the Fe(III)-Fe(II) metallocene case. The results provide support to a recent interpretation of the markedly faster self-exchange kinetics for the cobaltocenium-cobaltocene versus the ferrocenium-ferrocene redox couples in terms of differences in donor-acceptor orbital overlap.

As part of a detailed exploration of solvent dynamical effects in electron-transfer reactions, we have recently examined solvent-dependent rate parameters for the self exchange of cobaltocenium-cobaltocene ($\text{Cp}_2\text{Co}^{+/0}$, where Cp = cyclopentadiene) and for the decamethyl derivative ($\text{Cp-Me}_5)_2\text{Co}^{+/0}$ (where Cp-Me₅ = pentamethylcyclopentadiene).¹ A surprising finding from these studies is that the self-exchange rate constant, k_{ex} , in a given solvent is markedly (ca. tenfold) larger for $\text{Cp}_2\text{Co}^{+/0}$ and $(\text{Cp-Me}_5)_2\text{Co}^{+/0}$ relative to that for the ferrocene analogs, $\text{Cp}_2\text{Fe}^{+/0}$ and $(\text{Cp-Me}_5)_2\text{Fe}^{+/0}$, respectively. Since the nuclear reorganization parameters can be deduced to be essentially identical for the corresponding cobalt and iron systems, these rate differences were traced to dissimilarities in the nature and extent of donor-acceptor orbital overlap. This interpretation is consistent with the spatial properties of the orbitals involved; thus $\text{Cp}_2\text{Fe}^{+/0}$ electron exchange appears to employ either an $4e_2$ or $8a_{1g}$ orbital which are both strongly metal centered, whereas $\text{Cp}_2\text{Co}^{+/0}$ exchange apparently utilizes a markedly more ligand-centered $4e_{1g}$ orbital.^{1b} The greater facility with which electron exchange occurs for the cobaltocene versus ferrocene systems is attributed to a greater electronic transmission coefficient κ_{el} (i.e., higher electron-tunneling probability within the nuclear transition state) and/or to a correspondingly larger probability of forming reactive precursor complexes with the former reactions.^{1b}

Even though this apparent manifestation of donor-acceptor orbital coupling effects in thermal electron transfer is relatively unambiguous, it is desirable to obtain more direct experimental evidence. Such information is readily obtained in suitable cases from the characteristics of optical charge-transfer transitions within mixed-valence complexes.² Among the

systems of this type that have received detailed experimental scrutiny are biferrocene cations linked by a variety of bridging groups.^{3,4} Although the extent of mixed-valence electronic coupling is very sensitive to the structure of the groups linking the metallocene rings, the majority of these systems display near-infrared bands in solution at room temperature that are consistent with so-called "Class II" behavior, whereby the optical transition involves electron transfer between valence-trapped metal sites.³ In this case the extent of donor-acceptor coupling can be quantified by means of Hush theory.²⁻⁶

Given this favorable picture, we decided to examine the optical properties of analogous mixed-valence bicobaltocene species in order to ascertain if, and to what extent, greater donor-acceptor electronic coupling is indeed engendered in comparison with that for the corresponding biferrocene systems. We selected initially the bicobaltocene cation 1 in view of its simple structure, the availability of a synthetic procedure,⁷ and the solvent-dependent intervalence characterization afforded to the biferrocene cation, 2.⁵ The results of this study are presented here. We also compare briefly the optical properties of the corresponding bis-(fulvalene)-dicobalt and -diiron cations 3 and 4.

Experimental

Acetonitrile, propylene carbonate, dimethylformamide, and methylene chloride were obtained from Burdick and Jackson ("high purity") and benzonitrile from Fluka Chemicals. Acetonitrile and methylene chloride were distilled over P_2O_5 ; the other solvents were used as received. n-Tetrabutylammonium hexafluorophosphate (TBAH) was prepared by mixing

tetrabutylammonium iodide (Eastman Kodak) and ammonium hexafluorophosphate (Ozark-Mahoning) in acetone, and adding water to precipitate the TBAH. It was recrystallized from ethanol.

A solid mixture containing bicobaltocenium(III,III) hexafluorophosphate $[(Cp_2Co)_2(PF_6)_2]$, bis(fulvalene)-dicobalt(III,III) hexafluorophosphate, cobaltocenium hexafluorophosphate $[Cp_2Co \cdot PF_6]$, and higher order oligomers was prepared using the procedure of Davison and Smart.^{7b} We isolated a sample of $(Cp_2Co)_2(PF_6)_2$ by dissolving 1.0 g of the solid mixture in a minimum amount of acetonitrile and passing the solution over a 1.0 x 50 cm column of activated alumina. Elution with acetonitrile yielded four distinct bands; isolation and recrystallization (acetonitrile/ethyl ether) of the material from the second band gave a green powder, determined to be $(Cp_2Co)_2(PF_6)_2$ from the cyclic voltammetry (vide infra) and the proton NMR spectrum.

After dissolving $(Cp_2Co)_2(PF_6)_2$ in the desired solvent, it was reduced to $(Cp_2Co)_2^+$ by adding an appropriate quantity of cobaltocene in a nitrogen-atmosphere dry box. The solution was sealed into a 1 cm near-infrared quartz cuvette and the spectrum obtained immediately so as to minimize the extent of oxidation by trace oxygen and other impurities. These spectra were recorded on a Cary Model 17D spectrophotometer, typically scanned from 1700-800 nm. The bicobaltocene concentration was about 0.3-0.7 mM, adjusted so to yield a maximum absorbance of the intense near-infrared feature (vide infra) around 0.5. Although these solutions inevitably contained Cp_2Co^+ as well as small amounts of bis(fulvalene)dicobalt monocation, separate solutions of the latter species displayed no detectable absorbance in the wavelength region

(ca. 1300-1800 nm) over which the bicobaltocene near-infrared band was analyzed.

Cyclic voltammetric characterization was performed using a PAR Model 173/179 potentiostat driven by a PAR Model 175 Potential Programmer. All measurements were made at room temperature, $23 \pm 1^\circ\text{C}$.

Results and Discussion

Cathodic-anodic cyclic voltammograms for 1 mM $(\text{Cp}_2\text{Co})_2^{2+}$ at a gold electrode in acetonitrile containing 0.1 M TBAH consisted of a pair of reversible one-electron waves, yielding formal potentials, E_1^f and E_2^f , of -0.650 and -1.045 V versus a saturated calomel electrode (SCE). Bis(fulvalene)dicobalt dication, $(\text{BFD-Co})_2^{2+}$, exhibited similar voltammetric characteristics, with E_1^f and E_2^f equalling -0.10 and -1.03 V vs. SCE, respectively. This behavior is consistent with that reported previously for these species.⁷

The potential difference, $E_1^f - E_2^f = \Delta E_f$, provides a measure of the stability of the mixed-valence species with respect to the corresponding fully oxidized and reduced states (i.e., the comproportionation equilibrium⁸). These values are larger than observed with the corresponding diiron species; thus ΔE_f is 0.315 V for the biferrocene system, $(\text{Cp}_2\text{Fe})_2^{2+/+/0}$, (acetonitrile, 0.1 M TBAH^{3d}) and 0.59 V for bis(fulvalene)diiron, $(\text{BFD-Fe})_2^{2+/+/0}$, (acetonitrile, 0.1 M tetraethylammonium perchlorate⁹), as compared with 0.395 V and 0.93 V, respectively, for the corresponding dicobalt systems. The free energy of the comproportionation reaction, ΔG_C° , is related to ΔE_f by⁸

$$\Delta G_C^\circ = -0.5(F\Delta E_f - RT \ln 4) \quad (1)$$

This relation yields values of ΔG_c° equal to -4.15 and -3.2 kcal mol⁻¹ for the bicobaltocene and biferrocene systems, and -10.3 kcal mol⁻¹ and -6.4 kcal mol⁻¹ for bis(fulvalene)dicobalt and bis(fulvalene)diiron, respectively. The relatively greater stabilization afforded to the mixed-valence cobalt analogs is clearly evident in both cases.

Table I summarizes near-infrared spectral data for bicobaltocene cation, $(\text{Cp}_2\text{Co})_2^+$, in several solvents in comparison with some corresponding data for biferrocene cation, $(\text{Cp}_2\text{Fe})_2^+$, the latter taken from ref. 5. The solvents were selected so to yield a significant variation in the "solvent polarity" parameter, $(D_{\text{op}}^{-1} - D_s^{-1})$, where D_{op} and D_s are the optical and static dielectric constants, respectively. Two notable differences are seen in the form of the intervalence bands for this pair of systems, in that the band intensity, ϵ_{max} , for $(\text{Cp}_2\text{Co})_2^+$ is considerably (ca. 5 fold) greater and the band energy at maximum intensity, $\bar{\nu}_{\text{max}}$, is markedly less solvent dependent than that for $(\text{Cp}_2\text{Fe})_2^+$. In addition, the bandwidth, $\Delta\bar{\nu}_{1/2}$, is about 20% narrower for the former system. The variation of $\bar{\nu}_{\text{max}}$ with solvent in both cases is nonetheless qualitatively in accordance with the solvent continuum model in that a rough correlation with $(D_{\text{op}}^{-1} - D_s^{-1})$ is observed (Table I).

Previous discussions of the biferrocene mixed-valence system have concluded that while it can be considered to be valence trapped (i.e. Class II in the Robin-Day classification¹²), there is nonetheless substantial interaction between the Fe(III) and Fe(II) sites.^{3a,b,5} A useful parameter for estimating the extent of this coupling is the "electronic mixing coefficient" α , given by^{2,3a,6}

$$\alpha^2 = (4.2 \times 10^{-4}) \epsilon_{\text{max}} \Delta\bar{\nu}_{1/2} / \bar{\nu}_{\text{max}} d^2 \quad (2)$$

where d (Å) is the redox-site separation. Table II contains α values, along with ϵ_{\max} , $\bar{\nu}_{\max}$, and $\Delta\bar{\nu}_k$, for $(\text{Cp}_2\text{Co})_2^+$ in acetonitrile in comparison with the corresponding parameters for $(\text{Cp}_2\text{Fe})_2^+$ and a pair of related systems, bis(fulvalene) dicobalt $(\text{BFD-Co})^+$ and the corresponding iron dimer, $(\text{BFD-Fe})^+$ (Fig. 1). (See footnotes to Table II for literature sources.) Also listed for each system in Table II are calculated bandwidths, $\Delta\bar{\nu}_k(\text{calcd})$, where

$$\Delta\bar{\nu}_k(\text{calcd}) = (2310 \bar{\nu}_{\max})^{\frac{1}{2}} \text{ cm}^{-1} \quad (3)$$

This relation results from the Hush model for Class II systems.^{2,6a}

Inspection of these comparative data in Tables I and II provide a consistent picture attesting to the substantially greater metal-metal electronic coupling for the cobalt relative to the iron mixed-valence compounds. Thus, both the $(\text{Cp}_2\text{Co})_2^+$ and the $(\text{BFD-Co})^+$ systems display substantially larger α values and narrower bandwidths than the diiron analogs. While the observation that $\Delta\bar{\nu}_k > \Delta\bar{\nu}_k(\text{calcd})$ for $(\text{Cp}_2\text{Fe})_2^+$ is consistent with Class II behavior,^{6b} the opposite finding for $(\text{Cp}_2\text{Co})_2^+$ (Table II) suggests that there is sufficient electronic coupling with the latter system to place it on the Class II/III borderline. The relatively small solvent dependence of $\bar{\nu}_{\max}$ observed for $(\text{Cp}_2\text{Co})_2^+$ is also indicative of stronger donor-acceptor coupling than can be accommodated strictly in terms of Class II behavior.²

Especially since both $(\text{BFD-Co})^+$ and $(\text{BFD-Fe})^+$ also display essentially solvent-independent band energies,^{4a,b,11} comparison of α values for such delocalized systems^{4d} can be misleading since conventional interpretation of this parameter for intervalence transitions is linked to the Hush

model.^{2,6} Nevertheless, discussion of the overall trends in this and related quantities is likely to be qualitatively valid. The markedly larger α value, as well as the narrower bandwidth, observed for (BFD-Co)⁺ versus (BFD-Fe)⁺ (Table II) indicates that the additional metal-metal coupling provided by cobalt also applies to this strong-overlap, doubly-linked, structure (Fig. 1).

It is also interesting to compare the intervalence band parameters for (Cp₂Co)₂⁺ and (BFD-Fe)⁺. In spite of the additional electronic coupling engendered by the doubly-linked ring structure of the latter, the former system nonetheless appears to involve a greater extent of electron delocalization as signaled by substantially larger α value (Table II). These variations in the extent of electronic coupling brought about by metal substitution, as gauged by differences in α , are at least as large as those engendered by significant or even substantial alterations in the structure of the ring linkages.³⁻⁵

Estimates of the contribution of electronic delocalization, $\Delta G_{\text{del}}^{\circ}$, to $\Delta G_{\text{C}}^{\circ}$ can also be readily made, at least for Class II systems, from⁸

$$-\Delta G_{\text{del}}^{\circ} = \alpha^2 \bar{\nu}_{\text{max}} \quad (4)$$

This yields $\Delta G_{\text{del}}^{\circ}$ values of -0.55 and -0.2 kcal mol⁻¹ for (Cp₂Co)₂⁺ and (Cp₂Fe)₂⁺, respectively, in acetonitrile. An additional electrostatic contribution to $\Delta G_{\text{C}}^{\circ}$, $\Delta G_{\text{e}}^{\circ}$, can be estimated approximately to be -1.0 kcal mol⁻¹ under these conditions (acetonitrile, ionic strength 0.1 M).¹³ The substantial remaining components of the overall $\Delta G_{\text{C}}^{\circ}$ values, ca. -3.5 and -2 kcal mol⁻¹ for (Cp₂Co)₂⁺ and (Cp₂Fe)₂⁺, respectively, are presumably due to further stabilization of the mixed-valence species by inductive effects

via the bridging ligand (cf. bipyridyl diruthenium systems⁸).

These findings are therefore qualitatively consistent with the aforementioned interpretation of the larger rate constants for $\text{Cp}_2\text{Co}^{+/0}$ versus $\text{Cp}_2\text{Fe}^{+/0}$ self exchange in terms of electronic coupling effects. More quantitative comparisons between the bimolecular kinetic and intervalence optical systems, however, are precluded since the latter undoubtedly feature much stronger electronic interactions as a result of a direct linkage between the redox sites. Thus from the usual expression^{2,6} $H_{AB} = \alpha \bar{\nu}_{\text{max}}$, the electronic matrix coupling element H_{AB} is estimated to be roughly 3.2 and 1.7 kcal mol⁻¹ for $(\text{Cp}_2\text{Co})_2^+$ and $(\text{Cp}_2\text{Fe})_2^+$, respectively.¹⁶ Much smaller H_{AB} values, leading to weakly adiabatic or nonadiabatic electron transfer, are expected for thermally activated outer-sphere processes.¹⁷ Nevertheless, the present results do point clearly to the importance of the orbital symmetry in electron transfer via its influence on the extent of electronic coupling.

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13. This estimate is obtained by using the expression $-\Delta G_e^\circ = e^2/D_s d(1 + \kappa d)$, where e is the electronic charge, κ is the reciprocal Debye length, and d is the distance between the metal centers in the mixed-valence compound (see footnote e to Table II).

This relation is the Debye-Huckel expression¹⁴ for the work required to form a bimetallocene dication from two unipositive metallocene fragments. This represents the sole contribution to ΔG_e° since the corresponding electrostatic work for forming the neutral and monocation (i.e., mixed-valence) bimetallocene species are zero. Although Taube and coworkers have used a rather different ΔG_e° expression for various bipyridine-bridged diruthenium systems,¹⁵ the above relation is considered to be adequate for the present bimetallocene systems.

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16. This relationship will probably underestimate H_{AB} , at least for $(Cp_2Co)_2^+$, since this system lies on the Class II/III borderline; for Class III systems, $H_{AB} = \bar{\nu}_{max}/2$.
17. For example, Newton, M. D., J. Phys. Chem. 1986, 90, 3734.

TABLE I Comparison of Intervalence Transfer Bands for Bicobaltocene and Biferrocene Cations in Selected Solvents

Solvent ^a	$(D_{op}^{-1} - D_s^{-1})^b$	(Bicobaltocene) ⁺			(Biferrocene) ⁺		
		$\epsilon_{max}^{c,f}$ $M^{-1} cm^{-1}$	$\bar{\nu}_{max}^d$ $10^3 cm^{-1}$	$\Delta\bar{\nu}_h^{e,g}$ $10^3 cm^{-1}$	$\epsilon_{max}^{c,h}$ $M^{-1} cm^{-1}$	$\bar{\nu}_{max}^{d,h}$ $10^3 cm^{-1}$	$\Delta\bar{\nu}_h^{e,h}$ $10^3 cm^{-1}$
Acetonitrile	0.528	3500	6.58	3.28	~ 750 ⁱ	5.68	3.90
Propylene Carbonate	0.480		6.58	~ 3.3	650	5.57	4.12
DMF	0.463	3100	6.54				
Benzonitrile	0.390	3900	6.40				
Nitrobenzene	0.390				723	5.23	3.74
CH ₂ Cl ₂	0.380	4500	5.88		919	5.00	3.70

^a DMF - N,N-dimethylformamide; CH₂Cl₂ - dichloromethane.

^b D_{op} - optical dielectric constant; D_s - static (i.e., zero frequency) dielectric constant; values obtained from ref. 10.

^c Molar absorptivity at the band maximum.

^d Energy of band maximum.

^e Bandwidth at half height, obtained from high-wavelength portion as described in ref. 5.

^f Values reproducible to ca. 20-30%.

^g Values not given for several solvents due to solvent interference band wings and spectral instability.

^h Values extracted from ref. 5, unless otherwise noted.

ⁱ From ref. 3b.

TABLE II Intervalence Band and Related Parameters for some Dicobalt and Diiron Monocations in Acetonitrile

Compound	ϵ_{\max}^a $\text{M}^{-1} \text{ cm}^{-1}$	$\bar{\nu}_{\max}^b$ 10^3 cm^{-1}	$\Delta\bar{\nu}_h^c$ 10^3 cm^{-1}	$\Delta\bar{\nu}_h \text{ (calcd)}^d$ 10^3 cm^{-1}	α^e	Data source
$(\text{Cp}_2\text{Co})_2^+$	3500	6.58	3.28	3.90	0.17	f
$(\text{Cp}_2\text{Fe})_2^+$	750	5.68	3.90	3.62	0.09	g
$(\text{BFD-Co})^+$	7300	10.65	1.88	4.96	0.19	h
$(\text{BFD-Fe})^+$	1800	6.67	3.25	3.92	0.09	i

^a Molar absorptivity at band maximum.

^b Energy of band maximum.

^c Observed bandwidth at half height.

^d Bandwidth at half height, calculated from Eq. (3).

^e Electronic mixing coefficient, estimated using Eq. (2); d (metal-metal distance) values taken as 5 Å for dicobaltocene and biferrocene, and 4 Å for $(\text{BFD-Co})^+$ and $(\text{BFD-Fe})^+$ (after ref. 5).

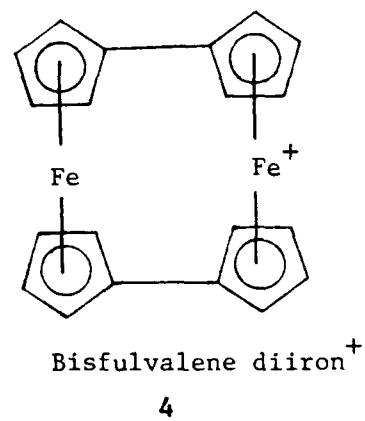
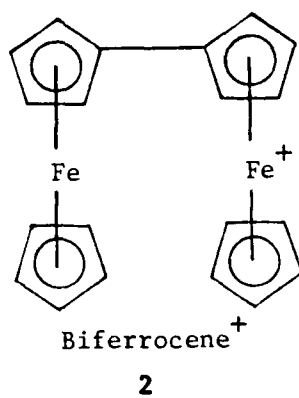
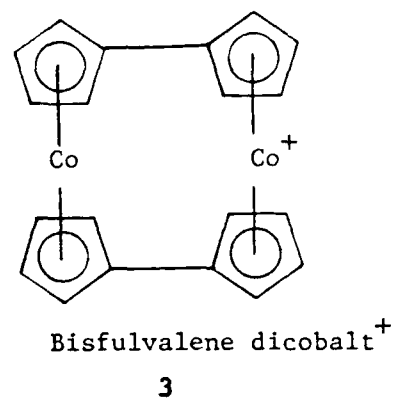
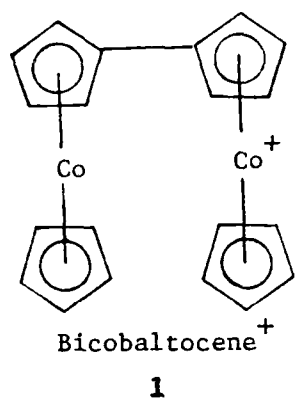
^f This work.

^g Ref. 5 (ϵ_{\max} from ref. 3b).

^h From Fig. 3 of ref. 11.

ⁱ Ref. 4a ($\Delta\bar{\nu}_h$ from ref. 5).

FIGURE 1



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